

The seasonal variations in nitric acid, nitrate, strong aerosol acidity, and ammonia in Warren, MI, was examined by Cadle (1985). The greatest variations was for ammonia, which was 8.5 times higher in summer than winter. The least variation was for particulate nitrate which had a summer maximum only 1.8 times higher than in spring minimum. It was noted that ammonium nitrate volatilization from filters and impactors can cause large errors in summertime measurements, but the errors are not significant during the winter.

The influence of local and regional sources on the concentration of particulate matter in urban and rural sites near Detroit, MI was investigated by Wolff et al. (1985). Analysis of spatial variations of the various particulate components revealed: (1) at all four sites the $PM_{2.5}$ was dominated by regional influences rather than local sources. The site in industrial sector had the largest impact of local sources, but even at his site the local influences appears to be smaller than the regional ones. (2) The regional influences were most pronounced on the sulfate levels which accounted for 40 to 50% of the $PM_{2.5}$. (3) Organic carbon compounds were the second most abundant $PM_{2.5}$ species accounting for 20 to 40% of the mass. Organic carbon seems to be controlled by both local and regional organic carbon influences. Vehicular emissions and possibly secondary reactions appear to affect the organic carbon concentrations. (4) Elemental carbon appears to be dominated by local emission. (5) PM_{Coarse} was dominated by local sources, but at the industrial site unknown non-crustal elements were significant components of coarse mass.

6.5.5 Subregional Aerosol Pattern in the Southwest

The arid southwestern U.S. includes metropolitan areas (El Paso, TX, Phoenix-Tucson, AZ) with modest industry and national parks (Grand Canyon) where the prevention of visibility degradation has been stated as a national goal. The southwest is a dusty region and much of the discussion below pertains to coarse particles and soil dust.

6.5.5.1 El Paso, Texas

The PM_{10} concentration in the El Paso, TX, subregion shows that the high and low concentration sites occur near each other (Figure 6-73a). This is an indication that local sources of PM_{10} with limited range of impact are important. In the El Paso, TX, subregion

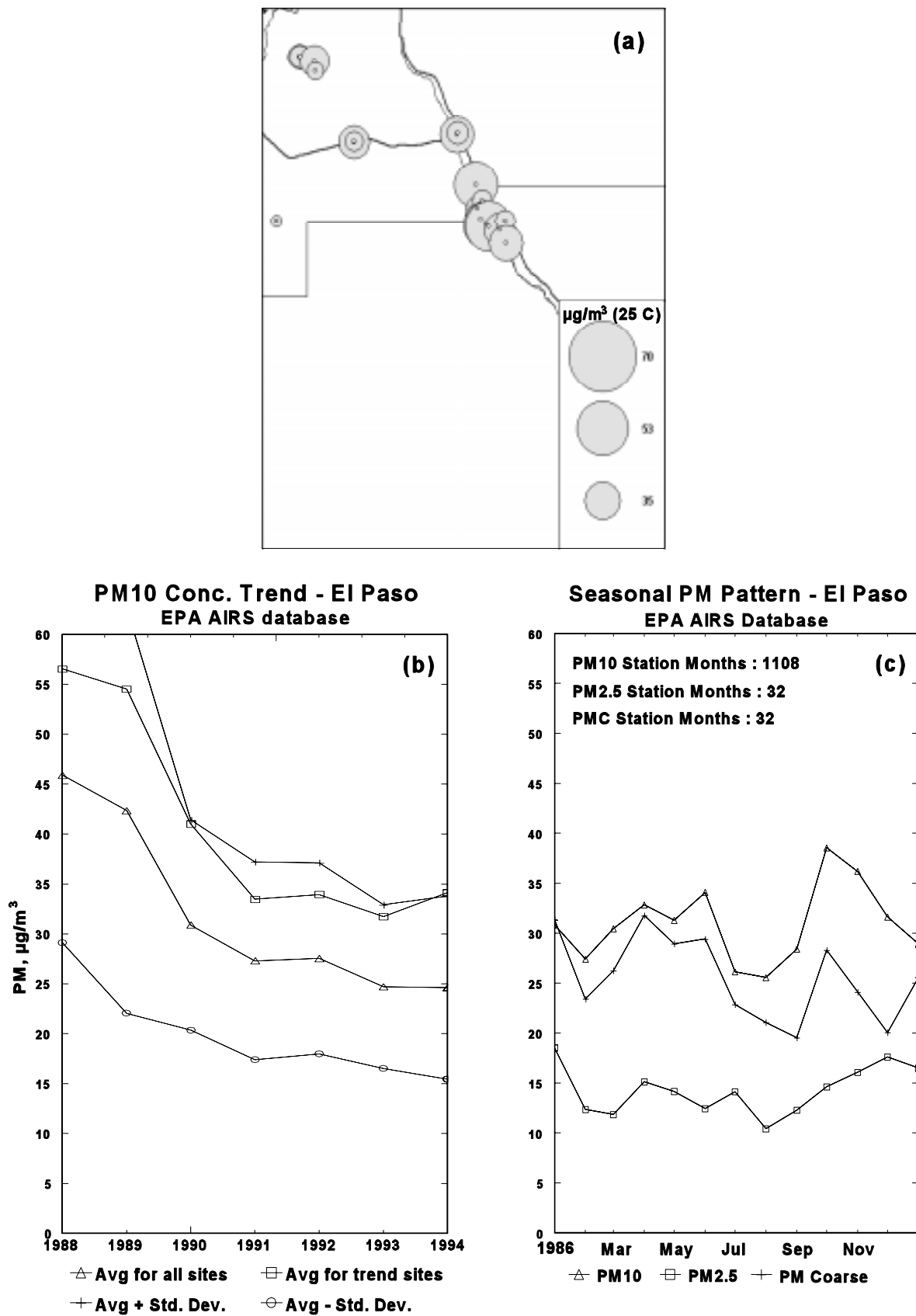


Figure 6-73. El Paso subregion: (a) aerosol concentration map, (b) trends, and (c) seasonal pattern .

there is a decrease in the annual average PM_{10} concentration between 1988 and 1994 from $46 \mu\text{g}/\text{m}^3$ to $25 \mu\text{g}/\text{m}^3$ for all sites and from $57 \mu\text{g}/\text{m}^3$ to $34 \mu\text{g}/\text{m}^3$ for trend sites (Figure 6-73b). The reductions were 46% for all sites and 40% for trend sites. This substantial reduction exceeds the PM_{10} decline over the entire southwestern region (Figure 6-46b).

The seasonality of PM_{10} over the El Paso, TX subregion (Figure 6-73c) is bimodal with peaks in the spring time, March through July, as well as another stronger peak, October through November. This double peak seasonality at El Paso, TX, also parallels the seasonality of the entire region. The concentration reduction in August which coincides with the arrival of moist flow from the Gulf of Mexico into states in the southwest (Figure 6-46d). Size segregated aerosol samples for El Paso, TX (AIRS #481410037) show that coarse particles dominate the PM_{10} concentrations, accounting for about 70% of the PM_{10} mass (Figure 6-74a). This is consistent with the important role of coarse particles over the arid Southwest. In comparison, size segregated data for San Antonio, TX (Figure 6-74b) located closer to the Gulf Coast in Texas, show that fine and coarse mass have comparable contributions, similar to Houston, TX.

6.5.5.2 Phoenix and Tucson, Arizona

The Phoenix-Tucson subregion (Figure 6-75a) shows a substantial PM_{10} concentration range. Samplers within the Phoenix or Tucson area indicate 2 to 3 times higher concentrations than the more remote sites, particularly the ones in the mountains. For the Phoenix-Tucson subregion there was a decrease in the annual average PM_{10} concentration between 1988 and 1993 from $39 \mu\text{g}/\text{m}^3$ to $28 \mu\text{g}/\text{m}^3$ for all sites and from $49 \mu\text{g}/\text{m}^3$ to $32 \mu\text{g}/\text{m}^3$ for trend sites (Figure 6-75b). The reductions were 28% for all sites and 35% for trend sites. The decrease in PM concentration were not monotonic. The average PM_{10} seasonality of the Phoenix-Tucson subregion (Figure 6-75c) shows the bimodal spring and fall peak pattern which is characteristic for the entire Southwest region.

During the Phoenix Urban Haze Pilot Study during the winter 1988 to 1989 (Frazier, 1989) a definite diurnal cycle in $PM_{2.5}$ concentrations was observed. The maximum, generally but not

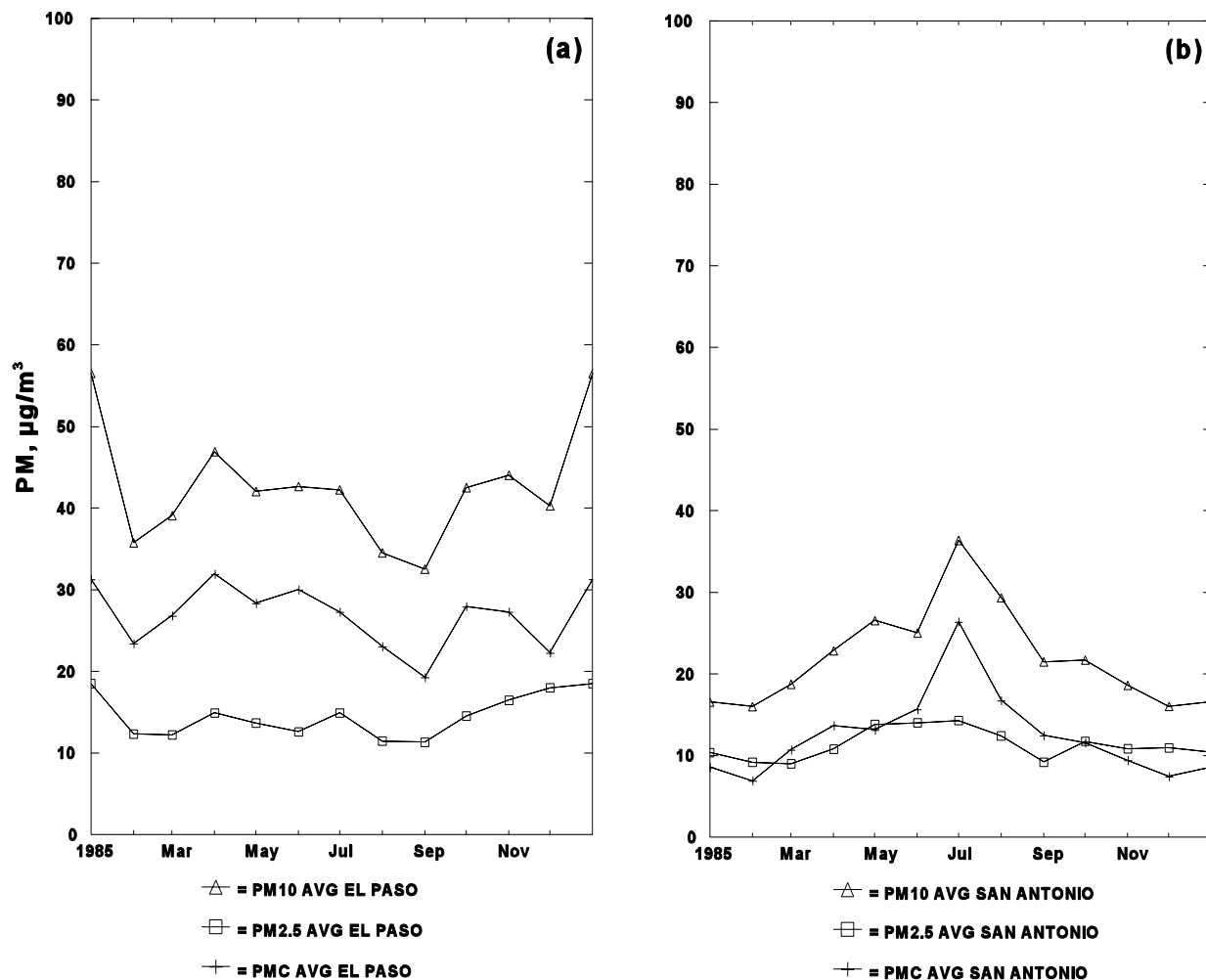


Figure 6-74a,b. Fine, coarse, and PM_{10} concentration patterns in El Paso and San Antonio.

always, occurred at night, which is consistent with the meteorological observations of poor dispersion and dilution.

The wintertime aerosol chemical pattern in Phoenix was reported by Chow et al. (1990) and Solomon and Moyers (1986). These investigators found fine particle crustal species, sulfates, nitrates, and organic and elemental carbon to be at least five times higher in concentration when comparing samples during a period of limited visibility to samples taken during good visibility.

A chemical characterization of wintertime fine particles in Phoenix, AZ (Solomon and Moyers, 1986) showed a dominance of organic carbon and nitrate aerosols. The composition in Phoenix is most like that of Denver, CO, a city which also experiences wintertime inversions

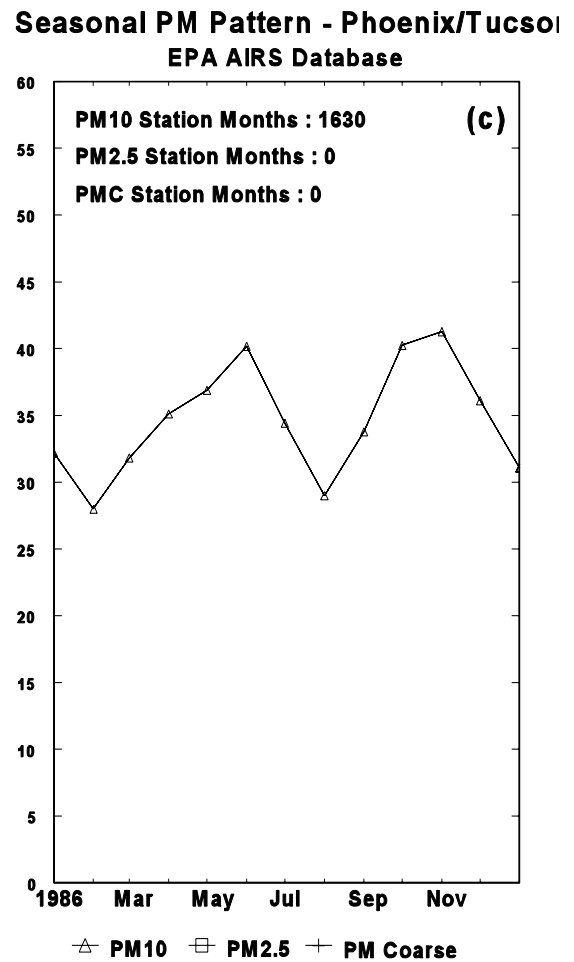
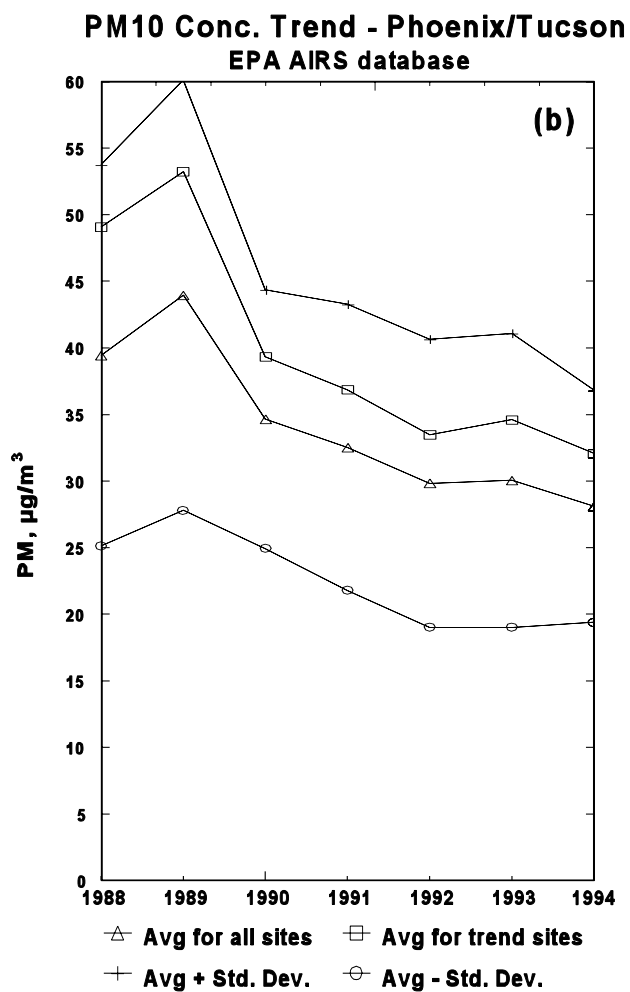
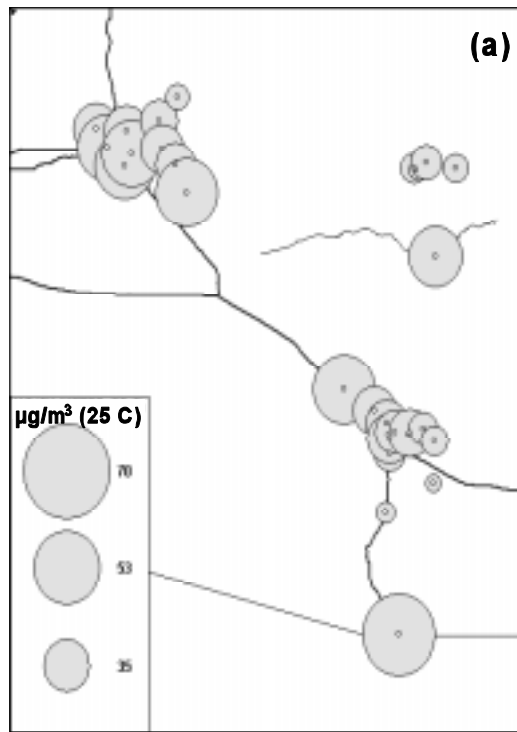


Figure 6-75. Phoenix-Tucson subregion: (a) aerosol concentration map, (b) trends, and (c) seasonal pattern.

(Pierson and Russell, 1979; Countess et al., 1980; Groblicki et al., 1981). In both cities, the average measured NO_3^- concentrations were about 1 to 2 times that of the average SO_4^{2-} concentration. In addition, the average SO_4^{2-} concentration measured in Phoenix was much lower than those observed at other locations throughout the U.S., but similar to the regional values observed in the Southwest (Moyers, 1982).

Wintertime PM_{10} and $\text{PM}_{2.5}$ chemical compositions and source contributions in Tucson, AZ (Chow et al., 1992a) show that the major contributors to the highest PM_{10} concentrations were geological material (>50%) and primary motor vehicle exhaust (> 30%) at three urban sampling sites. Secondary ammonium sulfate, secondary ammonium nitrate, and copper smelter aerosols were found to contribute less than 5% to elevated PM_{10} concentrations.

The OC/EC ratio was one to one at Phoenix sites. The average arsenic concentrations in Phoenix was four times higher than observed in other cities, which indicates the potential influence of Arizona smelters located within 100 miles of Phoenix. Average sulfate levels in Phoenix were higher than they were in Denver, which has less local emissions of SO_2 .

6.5.5.3 Grand Canyon National Park

McMurry and Zhang (1989) reported the size distribution of ambient organic and elemental carbon near the Grand Canyon and in the Los Angeles basin. Virtually all of the carbon was found in the submicron range, some below $0.1\ \mu\text{m}$. However, positive sampling artifacts for sub $0.1\ \mu\text{m}$ organics were considered significant.

At the Grand Canyon National Park, Zhang et al. (1994) showed that sulfates and carbonaceous particles were the major contributor to $\text{PM}_{2.5}$ particle scattering during the three winter months and that their contributions were comparable. Scattering by nitrates and soil dust was typically a factor of five to ten smaller. The low pressure impactor measurements also showed that sulfur size distributions vary considerably (0.07 to $0.66\ \mu\text{m}$).

6.5.6 Subregional Aerosol Pattern in the Northwest

The mountainous northwestern United States has many aerosol regions with different characteristics. The discussion below will examine South Lake Tahoe, as a case study for mountain-valley difference, Salt Lake City, UT, Denver, CO, Idaho-Montana sites, and several Washington-Oregon sites.

6.5.6.1 South Lake Tahoe

South Lake Tahoe IMPROVE monitoring site is located in a populated area on the south shore of Lake Tahoe. The Bliss State Park IMPROVE monitoring site is to the northwest, elevated (700ft) and removed from the populated areas. The pair of sites illustrates the populated area-remote difference in aerosol pattern. The aerosol and visibility at the two lake Tahoe sites were also examined (Molenar et al., 1994).

The concentration of all aerosol components is substantially higher on the south lake shore compared to the more remote site. The seasonality and chemical composition is also substantially different. The excess PM_{10} concentration at the S. Lake Tahoe site compared to Bliss State Park (Figure 6-76) is about $5 \mu g/m^3$ during the warm season, May through September, and it climbs to $28 \mu g/m^3$ excess in January. The factor of five seasonal modulation for valley excess PM_{10} is likely contributed by winter time emission sources, poor dispersion compared to the summer, as well as fog, all of which tend to enhance the aerosol formation. Fine and coarse particles contribute roughly equally to excess PM_{10} mass concentrations. However, fine particles contribute about 60% during the fall season and coarse particles prevail (>60%) during the spring. Both fine and coarse particles show a winter peak concentration.

The chemical composition of the valley excess fine particle mass concentration also shows a strong seasonality for organic carbon and elemental carbon. In fact, the excess organic carbon concentration in the winter ($13 \mu g/m^3$) is almost an order of magnitude higher than the summer values. The seasonal concentration of excess elemental carbon is similar to that of the organic carbon. However, the relative magnitude of organic carbon compared to elemental carbon is higher in the winter (factor of five) than in the summer (factor of two). The concentration of fine particle sulfate is virtually identical for South Lake Tahoe and Bliss State Park. This implies that the South Lake Tahoe aerosol sources do not contain sulfur. It is also worth noting that the excess fine particle soil at South Lake Tahoe is below $1 \mu g/m^3$, which is a small fraction of the coarse mass. Thus, the crustal component of the South Lake

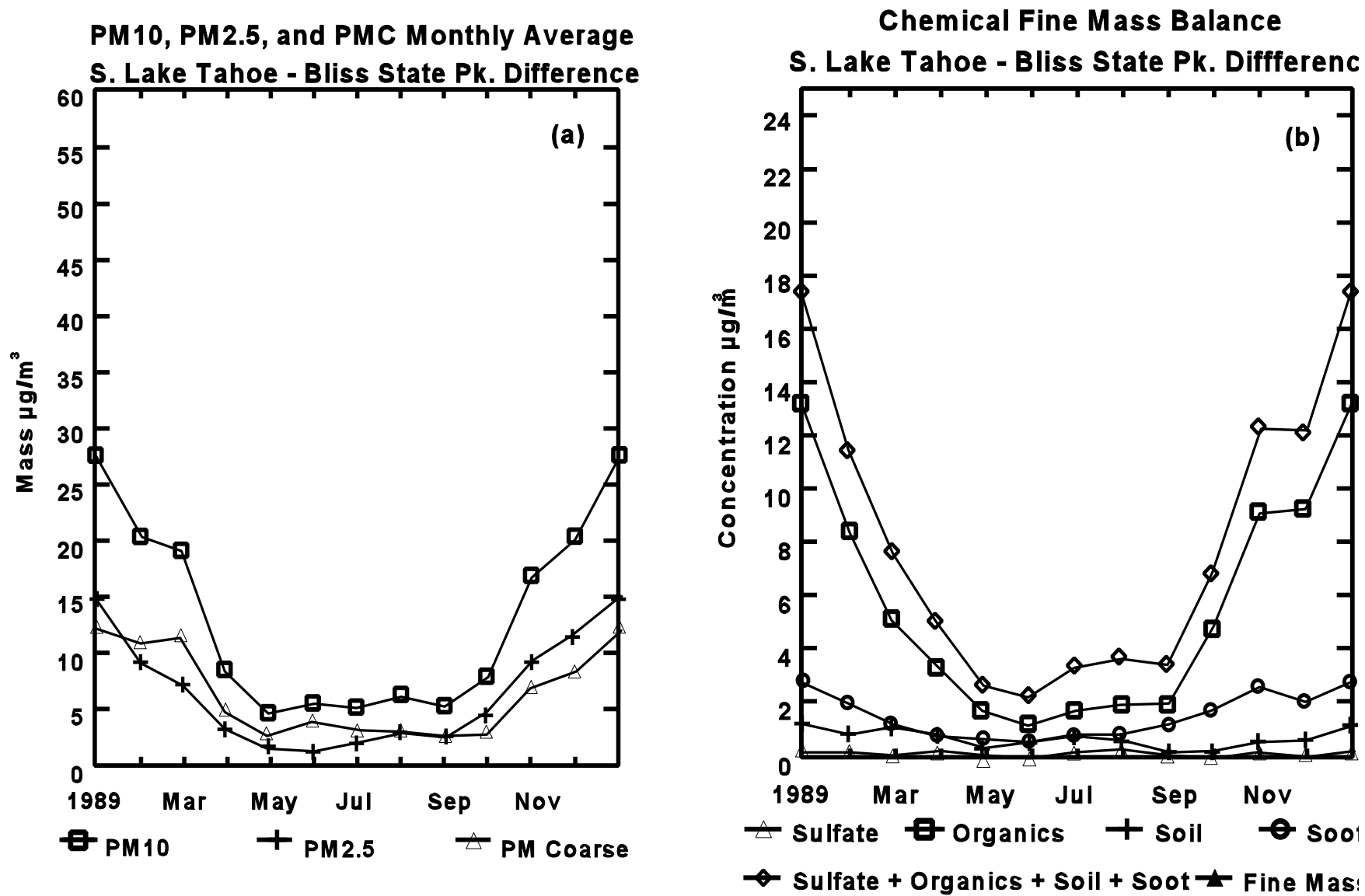


Figure 6-76. Excess aerosol concentration (a) and composition (b) at South Lake Tahoe compared to Bliss State Park.

Tahoe aerosol contributes to the coarse mass but not appreciably to the fine mass concentration.

In summary, there is a significant excess PM_{10} aerosol concentration at S. Lake Tahoe compared to the adjacent Bliss State Park remote site, particularly during the winter season ($28 \mu\text{g}/\text{m}^3$). The excess mass is about equally distributed between fine and coarse particles. The fine mass is largely composed of organics.

6.5.6.2 Salt Lake City, Utah, Subregion

Salt Lake City, Ogden, and Provo, UT, are part of an airshed that is confined by tall mountains to the East, limiting the dispersion by westerly winds.

The seasonal average PM_{10} concentration at three AIRS sites in Salt Lake City, Ogden, and Provo, UT, is shown in Figure 6-77b. All three sites show virtually identical seasonality, having peak concentrations during December through January. This confirms that the three sites belong to the same airshed with similar source pattern, meteorological dispersion and chemical transformation and removal processes.

During the 1988 to 1994 period there were overall decreases in the annual average PM_{10} for the Salt Lake City, UT subregion from $49 \mu\text{g}/\text{m}^3$ to $29 \mu\text{g}/\text{m}^3$ for all sites and from $54 \mu\text{g}/\text{m}^3$ to $30 \mu\text{g}/\text{m}^3$ for trend sites (Figure 6-77b). The reductions were 41% for all sites and 48% for trend sites. The trends were not monotonic, but showed substantial shifts upwards and downwards during the 1988 to 1994 period.

The size segregated fine and coarse concentration data exhibit a dynamic seasonal pattern. Fine particles clearly dominate the high winter concentrations reaching 40 to $50 \mu\text{g}/\text{m}^3$, compared to summer concentrations of $10 \mu\text{g}/\text{m}^3$. This magnitude of fine mass concentration is among the highest recorded in the AIRS data system. Coarse particles are less seasonal and they are more important during the dry summer season. The formation of sulfate and nitrate during winter inversion fogs near Salt Lake City, UT were studied by Mangelson et al. (1994).

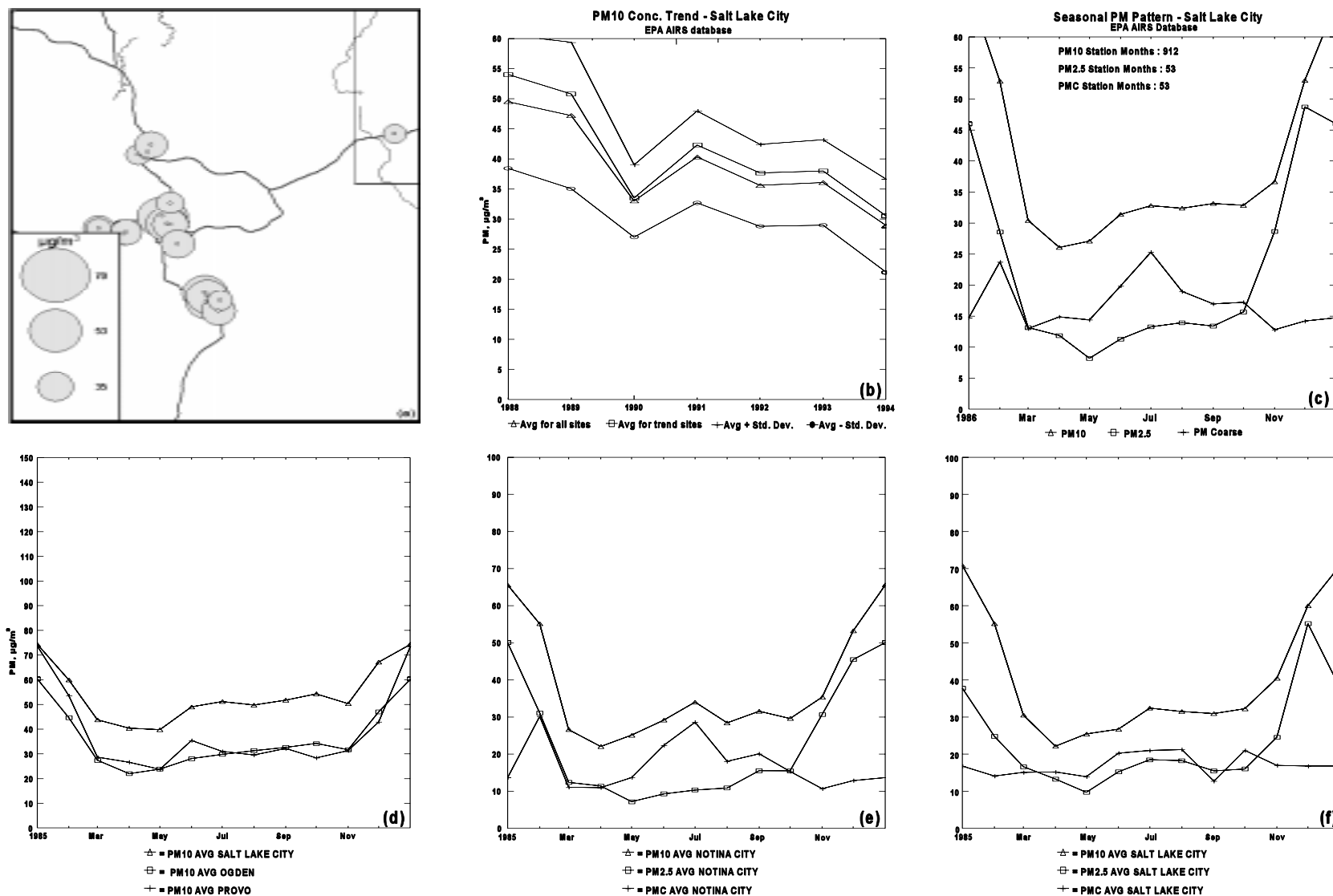


Figure 6-77. Salt Lake City region: (a) aerosol concentration map, (b) trends, (c) seasonal pattern, and (d,e,f) seasonal patterns at sites in or near Salt Lake City.

6.5.6.3 Denver, Colorado

The Denver brown cloud is a manifestation of high wintertime concentration of particles and gases. Several recent studies have focused on the characterization of the Denver brown cloud aerosols.

Size distribution measurements of winter Denver aerosol (Countess et al., 1981) show that on high pollution days that the mass median aerodynamic diameter of the accumulation mode aerosol was about $0.31\ \mu\text{m}$ with $\sigma_g \pm 2.0$. Wolff et al. (1981) found that on the average motor vehicles were responsible for 27% of the elemental carbon while wood burning was responsible for 39% of the elemental carbon.

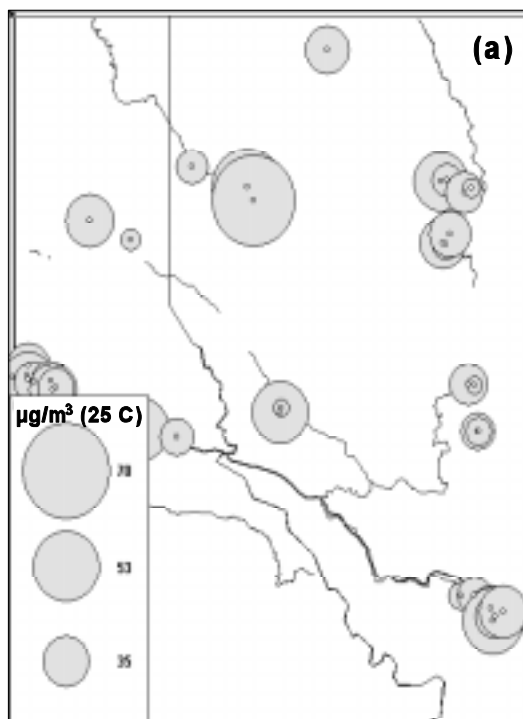
The chemical composition of wintertime Denver fine aerosol mass ($16.4\ \mu\text{g}/\text{m}^3$) (Sloane et al., 1991) shows the dominance of total carbon consisting of organic carbon ($8.1\ \mu\text{g}/\text{m}^3$) and elemental carbon ($2.6\ \mu\text{g}/\text{m}^3$) over sulfate ($1.2\ \mu\text{g}/\text{m}^3$) and nitrate ($3.4\ \mu\text{g}/\text{m}^3$). The fine particle size distribution of sulfate and nitrates were bimodal.

6.5.6.4 Northern Idaho-Western Montana Subregion

The mountainous northern Idaho and western Montana subregion is characterized by deep valleys and the absence of major industrial sources or large urban-metropolitan areas. Nevertheless, PM_{10} monitoring sites in northern Idaho and western Montana report concentrations that are among the highest in the nation, as illustrated in Figure 6-78a, while nearby sites are among the lowest. The large spatial concentration variability is evidently related to the rugged terrain. Most of the monitoring sites are located in the flat valleys.

In the northern Idaho-western Montana subregion there was a decrease in the annual average PM_{10} concentrations between 1988 and 1993 from $41\ \mu\text{g}/\text{m}^3$ to $30\ \mu\text{g}/\text{m}^3$ for all sites and from $40\ \mu\text{g}/\text{m}^3$ to $31\ \mu\text{g}/\text{m}^3$ for trend sites. The reductions were 27% for all sites and 23% for trend sites (Figure 6-78b). The average seasonality of the subregion is strongly winter peaked (Figure 6-78c) with a factor of two modulation between 25 and $45\ \mu\text{g}/\text{m}^3$.

The high spatial variability is illustrated in an example from northern Idaho (Figure 6-79a). Three sites in Missoula, MT, show winter monthly averaged peak concentrations from less than 40 to more than $100\ \mu\text{g}/\text{m}^3$. This is higher than the monthly average PM_{10} concentration anywhere in the eastern U.S. The site closest to the city center



PM10 Conc. Trend - N. Idaho/NW Montana EPA AIRS database **Seasonal PM Pattern - Idaho/Montana EPA AIRS Database**

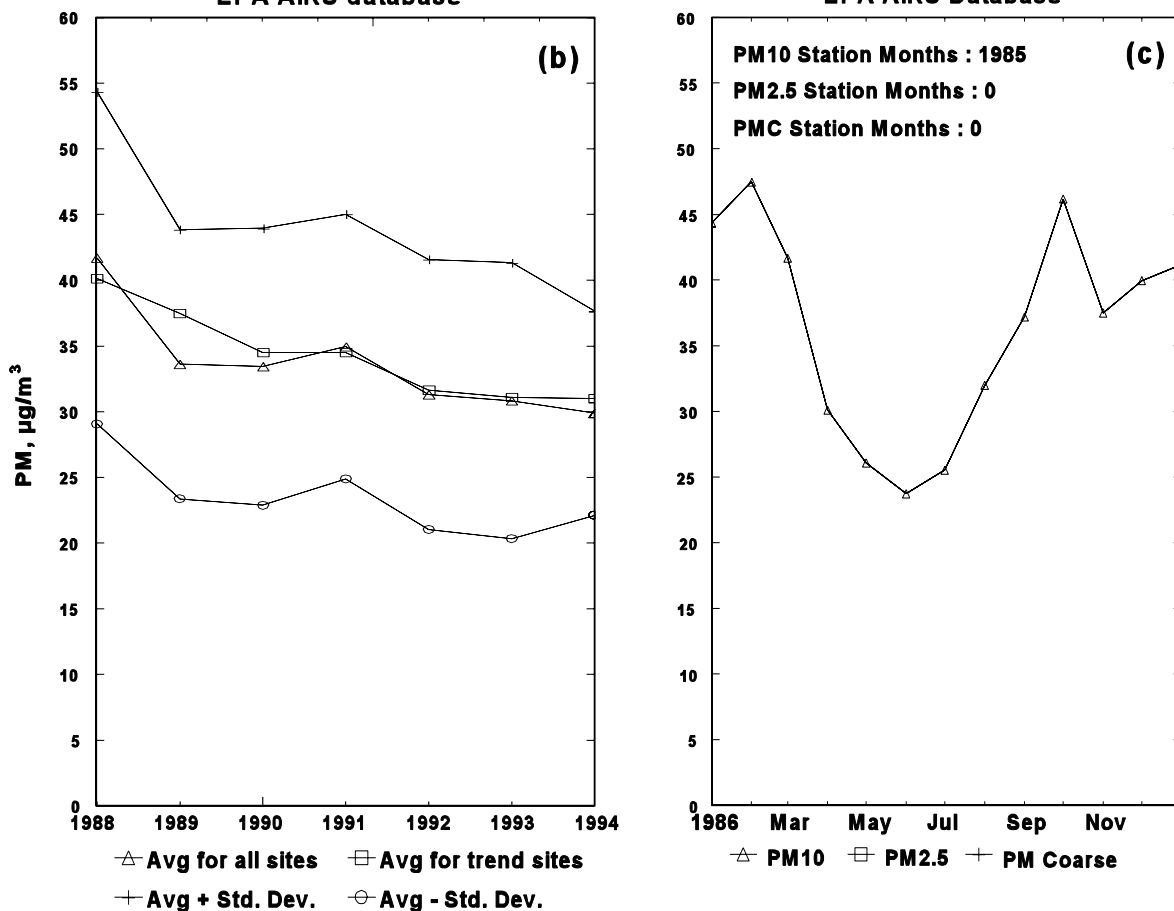


Figure 6-78. Northern Idaho-Northwestern Montana subregion: (a) aerosol concentration map, (b) trends, and (c) seasonal pattern.

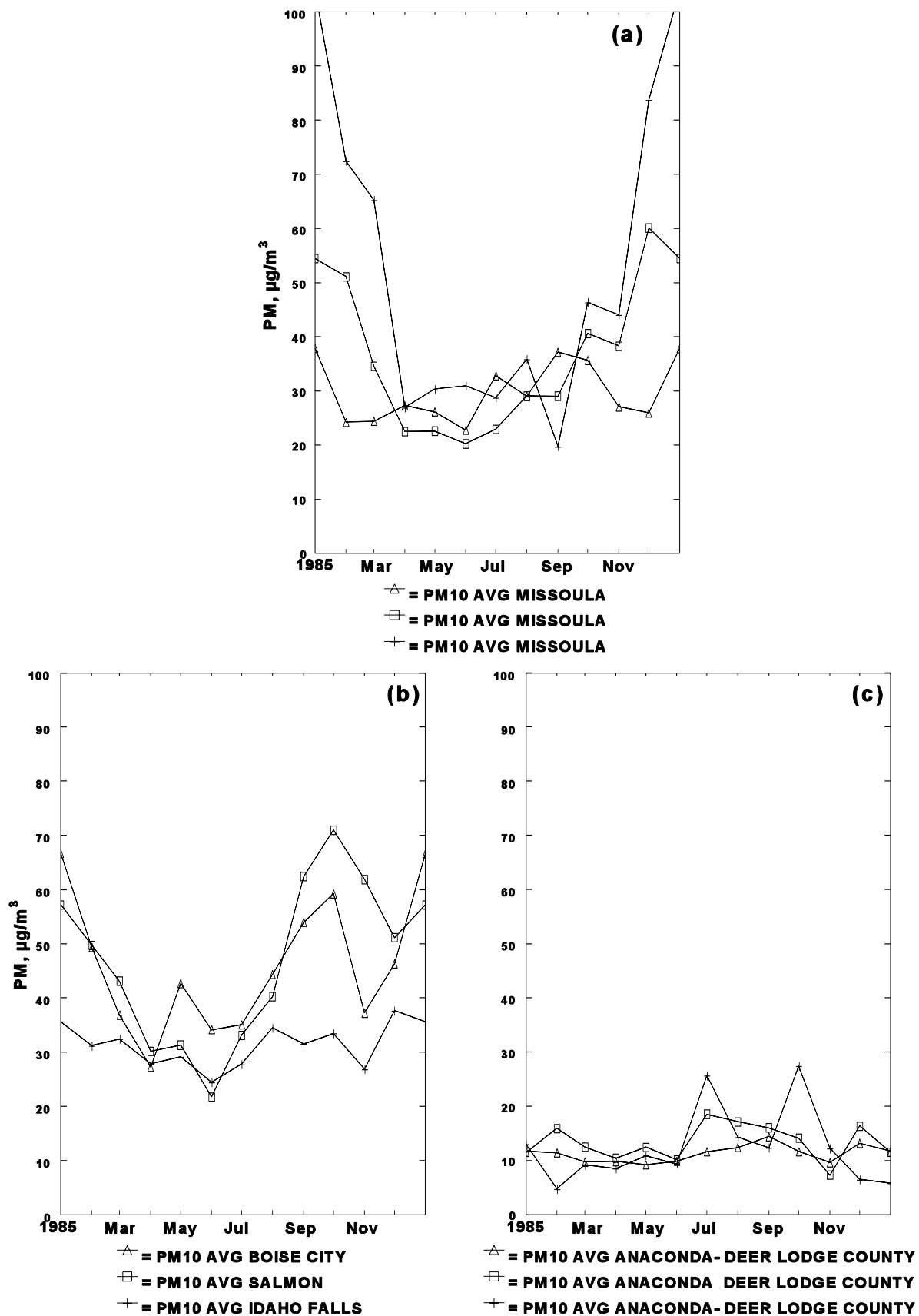


Figure 6-79a,b,c. PM_{10} concentration patterns at sites in the Northern Idaho-Northwestern Montana subregion.

shows the highest winter peak ($>100 \mu\text{g}/\text{m}^3$), but has summer values that are comparable to the other two sites. It is evident that in Missoula, MT, high concentration gradients exist between the populated areas and remote sites. Boise and Salmon, ID (Figure 6-79b) also show elevated PM_{10} concentrations during the cold season. Idaho Falls, ID, on the other hand, is seasonally uniform at about $30 \mu\text{g}/\text{m}^3$, which is comparable to the lowest Missoula, MT, site.

Unusually low PM_{10} concentrations of $10 \mu\text{g}/\text{m}^3$ are reported at three PM_{10} monitoring sites near Anaconda-Deer, ID (Figure 6-79c). This result is unexpected because the sites are in a valley. The characteristic winter peak is completely absent. This suggests that pristine, low, PM_{10} sites can exist in the northwestern valleys, and hence the region is not uniformly covered by wintertime haze or smoke.

6.5.6.5 Washington-Oregon Subregion

The Pacific Northwest is also a mountainous subregion that exhibits unique aerosol characteristics. During 1988 to 1994, there were decreases in the annual average PM_{10} concentrations for the Washington-Oregon subregion from $36 \mu\text{g}/\text{m}^3$ to $26 \mu\text{g}/\text{m}^3$ for all sites and from $39 \mu\text{g}/\text{m}^3$ to $28 \mu\text{g}/\text{m}^3$ for trend sites. The reductions were 28% for both all sites and trend sites. The subregion shows a strong seasonality with a winter peak due to $\text{PM}_{2.5}$ (Figure 6-80b). PM_{10} monitoring sites in Seattle, Bellevue, and Tacoma, WA (Figure 6-80d), show relatively low concentrations and a lower seasonality although higher values occur in the winter. A much more pronounced seasonality of PM_{10} concentrations is recorded in southern Oregon. Medford, Grants Pass, and Klamath Falls, OR (Figure 6-80e) evidently belong to an airshed in which emissions, dispersion, and aerosol formation mechanisms are conducive to the formation of winter time aerosol (60 to $80 \mu\text{g}/\text{m}^3$).

Fine and coarse particle data collected over a limited period in 1987 show that the winter peak of PM_{10} is entirely due to the strong winter peak of fine particle mass (50 to $100 \mu\text{g}/\text{m}^3$). Coarse mass, on the other hand, is seasonally invariant at about 10 to $20 \mu\text{g}/\text{m}^3$. Fine particles clearly are responsible for the winter peak. This is somewhat different from the observations at South Lake Tahoe, where the winter peak was attributed to both fine and coarse particles.

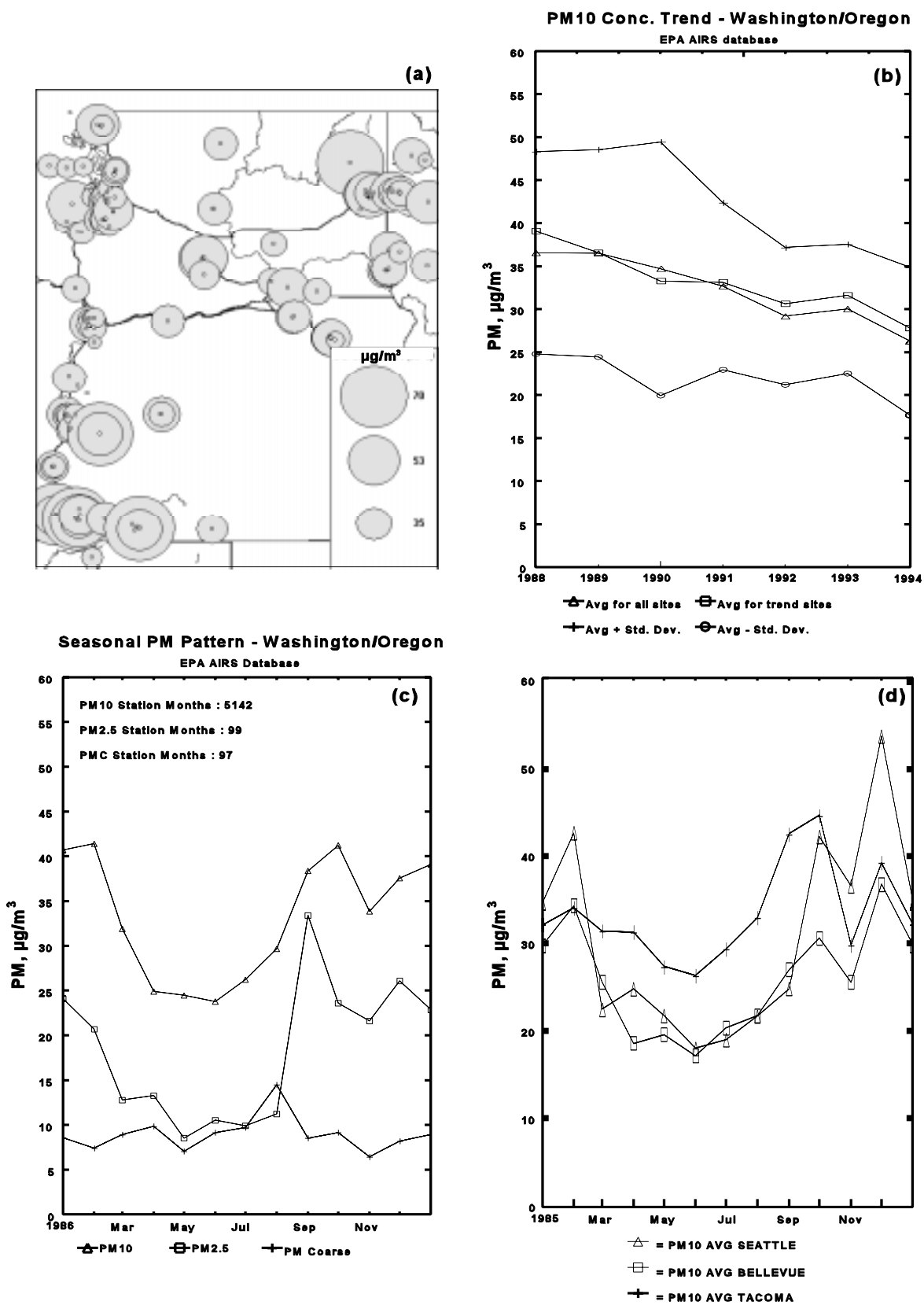


Figure 6-80a,b,c,d,e,f,g,h. Aerosol concentration patterns in Washington State and Oregon.

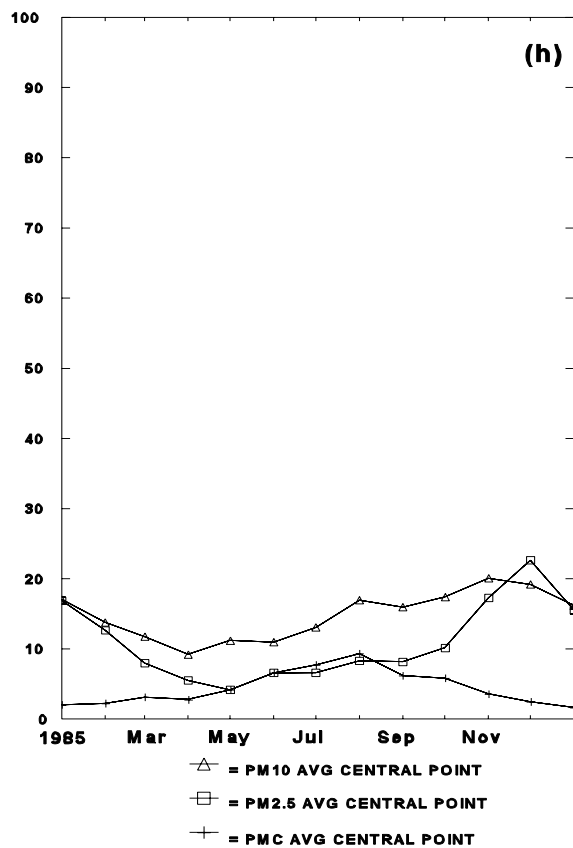
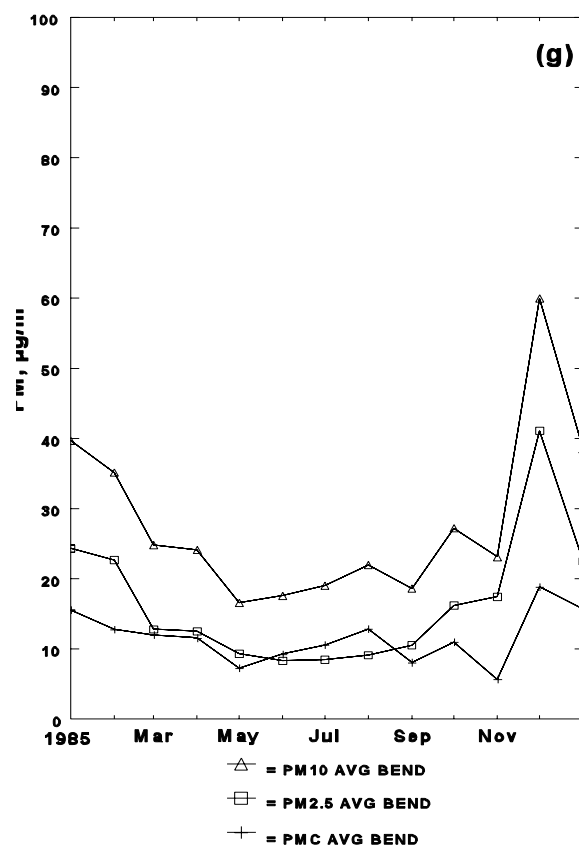
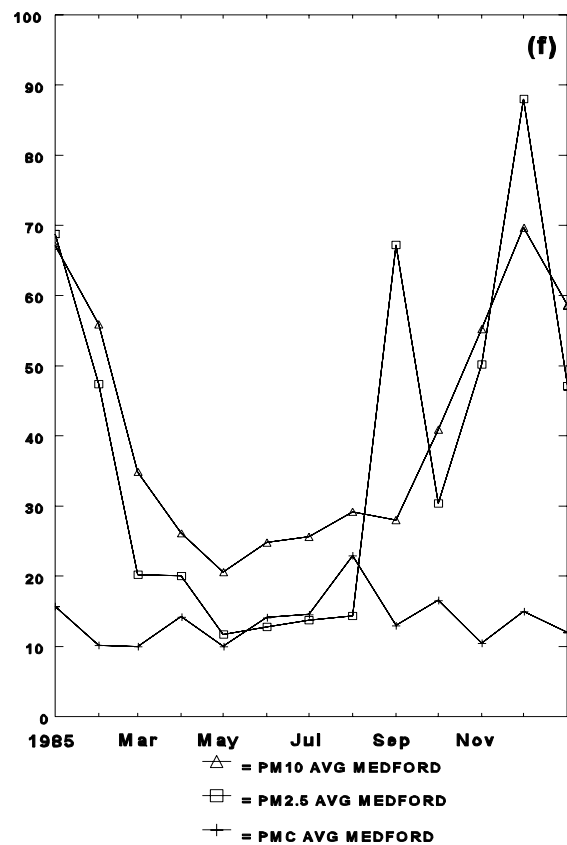
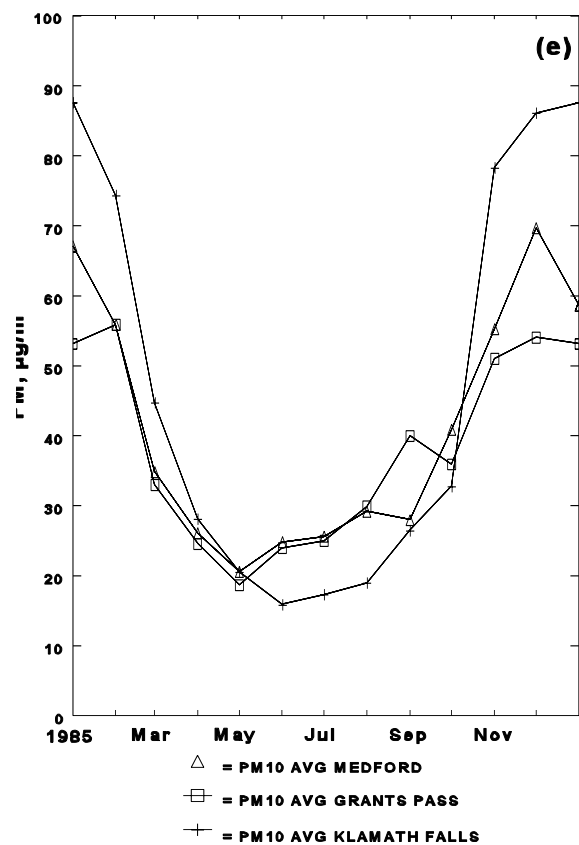


Figure 6-80 (cont'd). Aerosol concentration patterns in Washington State and Oregon.

The size segregated aerosol data for Bend and Central Point, OR (Figure 6-80g,h), show diminishing concentrations compared to Medford (Figure 6-80f), where the reduction of PM_{10} is mainly due to the decrease of the fine particle mass during the winter season.

In Portland, OR, carbonaceous aerosol was found to account for about 50% of fine aerosol mass (Shah et al., 1984).

6.5.6.6 Other Northwestern Locations

Dresser (1988) investigated the winter PM_{10} concentrations in a small ski resort town, Telluride, CO, and found that the street dirt and sand are major contributors, particularly during the dry post snow period. Wintertime source apportionment attributed to 45% of the PM_{10} mass to residential wood combustion in San Jose, CA (Chow et al., 1995a).

6.5.7 Subregional Aerosol Pattern in Southern California

The southern California region has two subregions, the San Joaquin Valley and the Los Angeles-South Coast Air Basin, discussed separately in sections below.

6.5.7.1 San Joaquin Basin

The wide air basin between the coastal mountain ranges of California to the west and the Sierra Nevada Mountains to the east shows reasonably uniform PM_{10} concentrations as indicated on the map (Figure 6-81a). There is evidence of PM_{10} concentration reduction but the trend is not conclusive (Figure 6-81b). The seasonal modulation amplitude over the San Joaquin Valley (Figure 6-81c) is about factor of 2.5 between the low spring concentration 30 to 35 $\mu\text{g}/\text{m}^3$, and high fall concentration (60 to 70 $\mu\text{g}/\text{m}^3$). The unique feature of this seasonality is the fall peak which differs from the summer peak in the eastern United States and winter peak over the mountainous northwestern states.

The AIRS database contains valuable size segregated fine and coarse particle concentration data within the San Joaquin Valley, as shown in Figure 6-82 for Fresno, Madera, Visalia, and Bakersfield, CA. These monitoring sites show virtually identical concentration patterns for fine and coarse mass. Both coarse and fine particles are important contributors to the San Joaquin Valley PM_{10} aerosol. However, their respective prevalence is phase shifted. Fine particles are

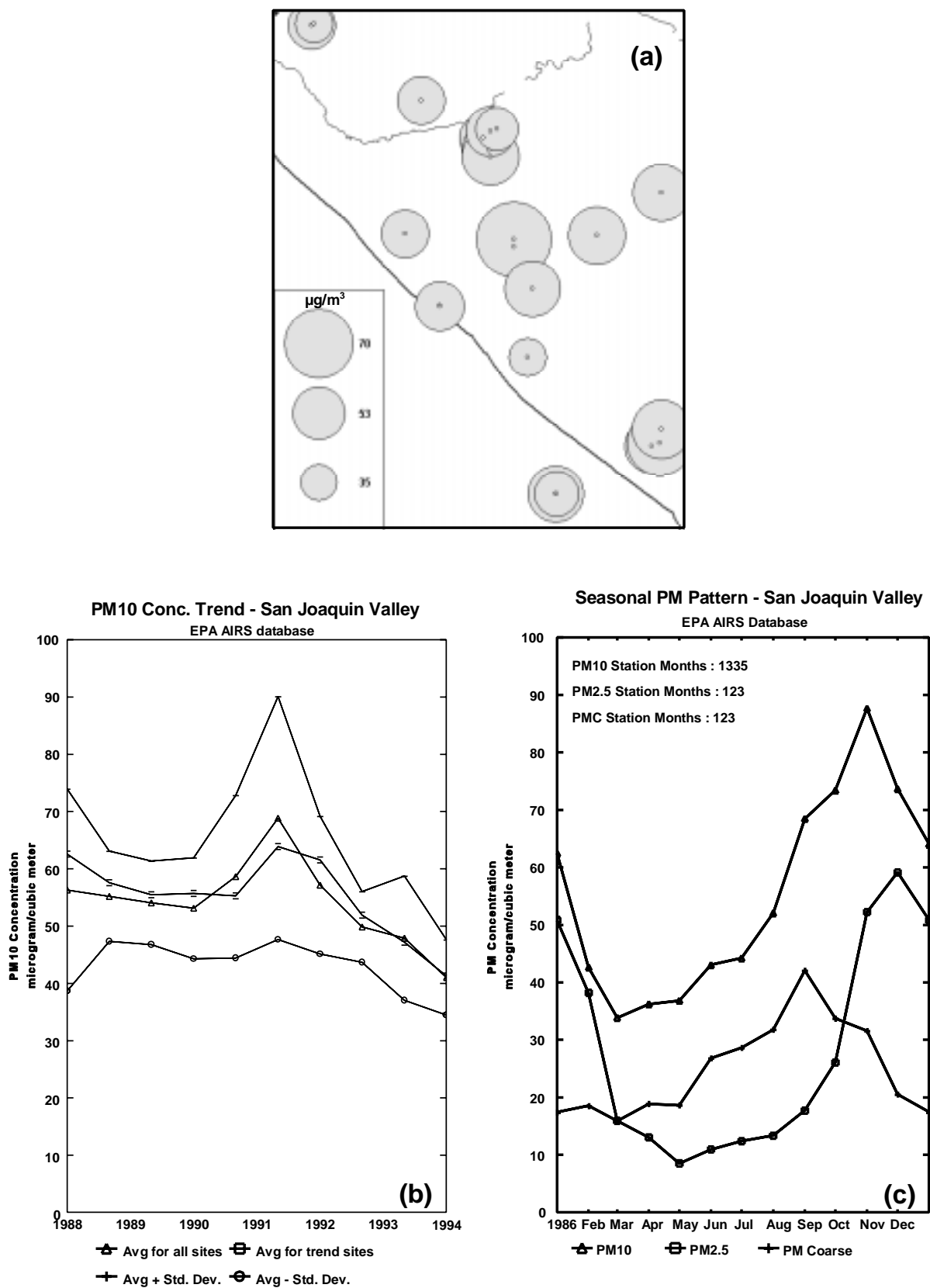


Figure 6-81. San Joaquin Valley: aerosol concentration map, trends, and seasonal pattern.

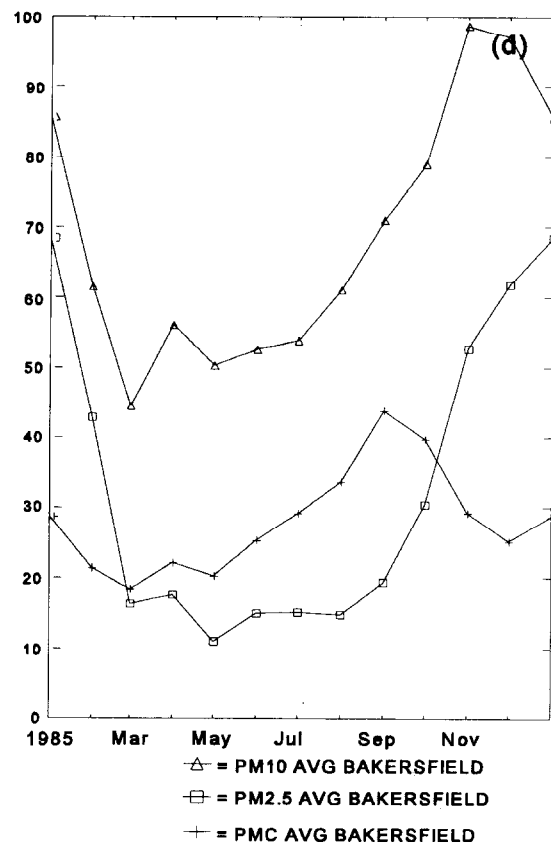
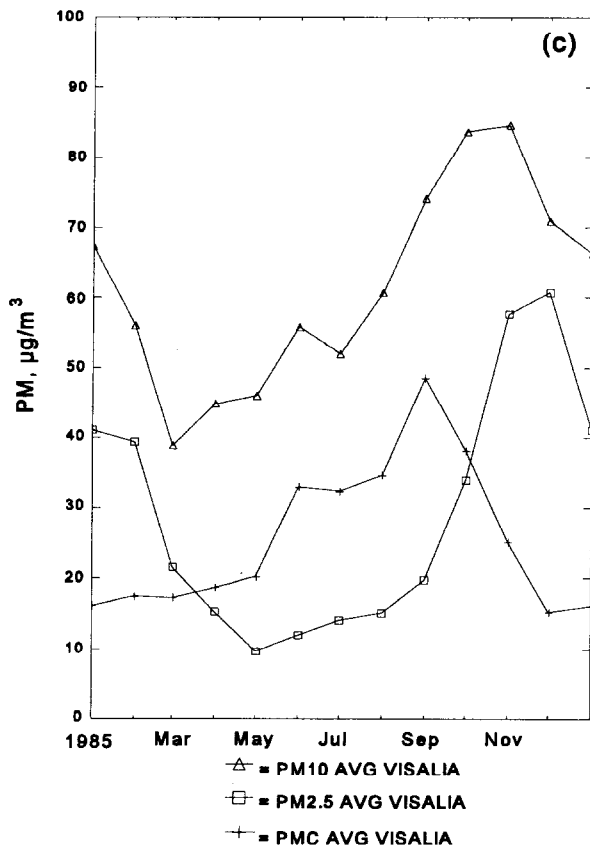
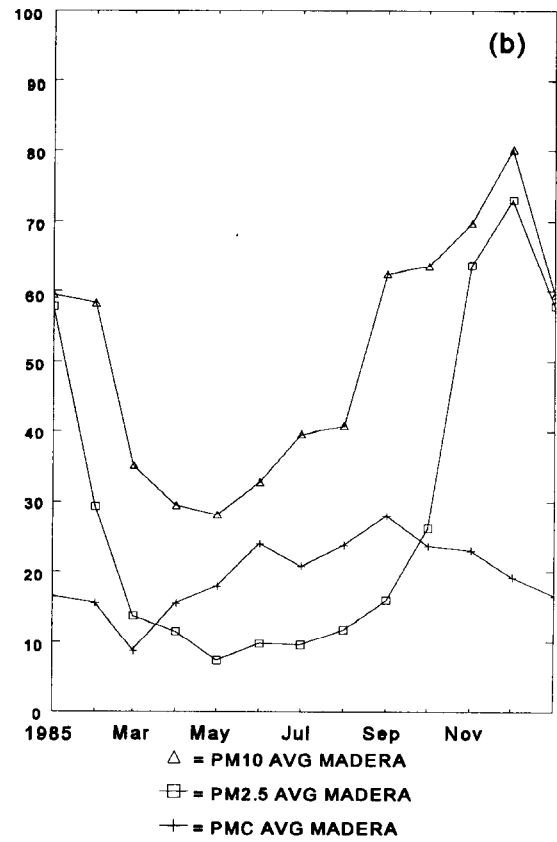
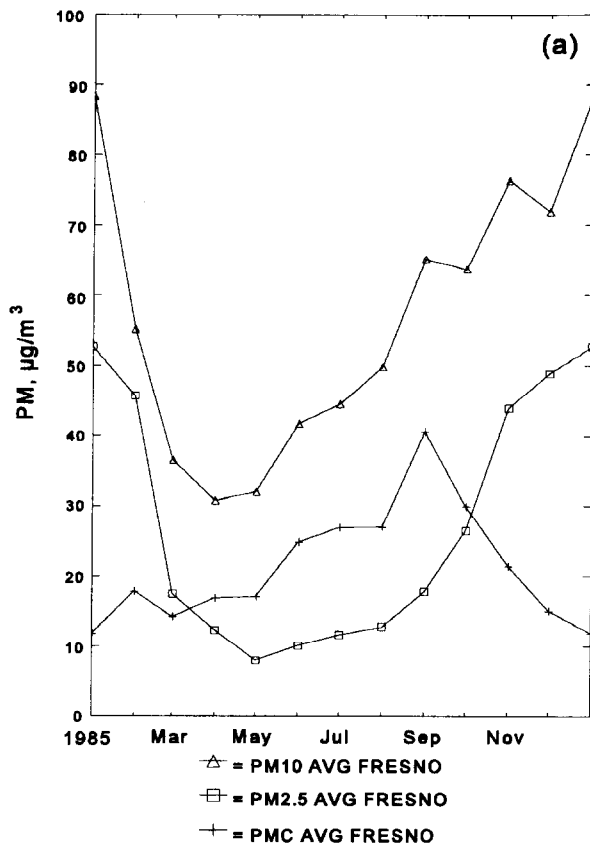


Figure 6-82. Fine, coarse, and PM₁₀ seasonal patterns in the San Joaquin Valley.

most important during the November through February winter season, while coarse particles prevail during April through September. In November, both coarse and fine particles contribute to the seasonal peak of PM_{10} . During March through May, neither fine or coarse particles are abundant and the PM_{10} concentration is lowest during the spring season.

The temporal dynamics of the emissions, ventilation and aerosol formation in the San Joaquin Valley has been the subject of detailed aerosol monitoring, and source apportionment studies.

The aerosol composition at nonurban sites (Chow et al., 1995b) provides further characteristics of the central California aerosol pattern (Figure 6-82). A PM_{10} aerosol study was carried out at six sites in California's San Joaquin Valley from 14 June 1988 to 9 June 1989, as part of the 1988 to 1989 Valley Air Quality Study (VAQS). Concentrations of PM_{10} and $PM_{2.5}$ mass, organic and elemental carbon, nitrate, sulfate, ammonium, and elements were determined in 24-h aerosol samples collected at three urban (Stockton, Fresno, Bakersfield) and three non-urban (Crows Landing, Fellows, Kern Wildlife Refuge) locations (Chow et al., 1993a). The VAQS data indicate the federal 24-h PM_{10} standard of $150 \mu\text{g}/\text{m}^3$ was exceeded at four out of the six sites and for reasons which differ by season and by spatial region of influence. The annual average source contributions to PM_{10} at Bakersfield, the site with the highest annual average, were 54% from primary geological material, 15% from secondary ammonium nitrate, 10 % from primary motor vehicle exhaust, 8% from primary construction, the remaining 4% is unexplained. The results of the source apportionment at all sites show that geological contributions dominate in summer and fall months, while secondary ammonium nitrate contributions derived from direct emissions of ammonia and oxides of nitrogen from agricultural activities and engine exhaust are largest during winter months. (Chow et al., 1992b).

6.5.7.2 Los Angeles-South Coast Air Basin-Southeastern Desert Air Basin

The Los Angeles basin is confined by the San Gabriel Mountains which limit the ventilation during westerly winds. Intensive emissions from automotive and industrial sources produce the Los Angeles smog with numerous secondary photochemical reaction products from primary emissions. The map of the Los Angeles subregion shows (Figure 6-83a) the

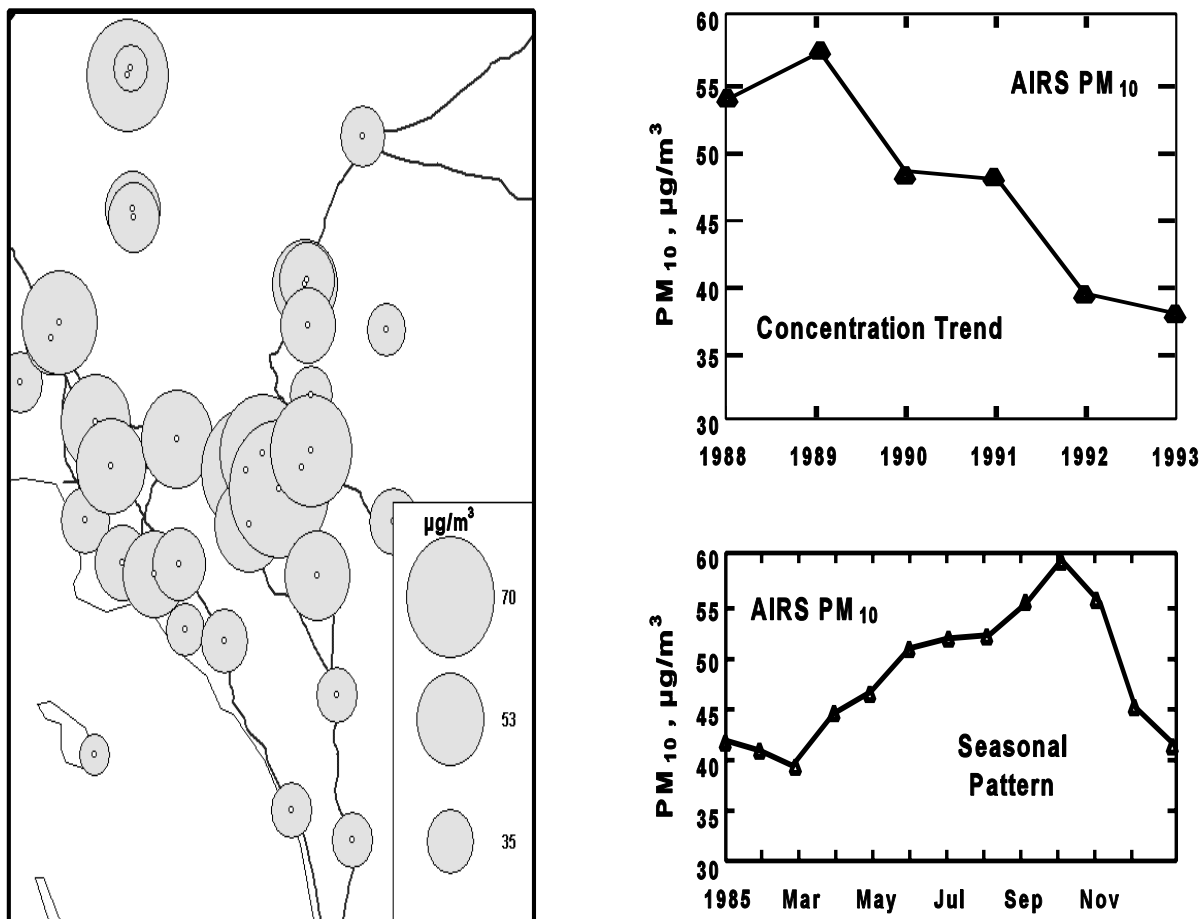


Figure 6-83. Los Angeles: (a) aerosol concentration map, (b) trends, and (c) seasonal pattern.

magnitude of PM₁₀ concentrations for individual monitoring stations. Isopleths of PM₁₀ concentration for 1992 are consistent with these results showing the highest PM₁₀ concentrations are measured in the center of the LA basin with the lower concentration of PM₁₀ near the ocean and out in the desert and the mountains (Hoggan et al., 1993).

There has been a substantial reduction of subregion average PM₁₀ concentration from 1988 to 1993 from 54 $\mu\text{g}/\text{m}^3$ down to 38 $\mu\text{g}/\text{m}^3$ (Figure 6-83b), a reduction of 30%. The seasonality of the basin averaged PM₁₀ concentration shows a 50% amplitude, with the peak concentration (60 $\mu\text{g}/\text{m}^3$) during October and the lowest values (40 $\mu\text{g}/\text{m}^3$) during January through March (Figure 6-83c). Hence, this fall peaked seasonality is similar to the fall peak over the San Joaquin Valley.

The PM_{10} air quality in the California South Coast Air Basin (CSCAB) and to a limited extent in the Southeastern Desert Air Basin have been analyzed for the 1985 to 1992 period (Hoggan et al., 1993). Although a larger number of monitoring stations exist in more recent years, the analysis involved only the monitoring stations with complete data in Long Beach, Burbank, El Toro, Ontario, Rubidoux, Banning, and Indio. Measurements in downtown Los Angeles also are used in parts of the analysis (Hoggan et al., 1993). The annual average PM_{10} trend line for 1985 to 1992 showed a statistical significant trend downwards with the decrease averaging 3% per year. The sulfate and nitrate also were measured and they accounted for about one-third of the decrease in PM_{10} . The decreases between 1989 and 1993 for this set of stations were smaller than for the larger group of stations (Figure 6-83b). There was a statistically significant decrease (0.05 level of significance) at Burbank, Long Beach, Rubidoux, and Banning. Use of both a decision tree analysis and a multiple linear regression analysis showed that the temperature at 850 mb, a measure of mass stability, was an important variable associated with PM_{10} in the CSCAB. Use of this variable suggests that the observed decreases in annual average PM_{10} concentrations between 1987 and 1992 are not an artifact of meteorology. A more detailed discussion of these analyses as related to various aspects of meteorology is given (Hoggan et al., 1993).

The diurnal patterns of PM_{10} also are discussed (Hoggan et al., 1993). The Rubidoux monitoring station showed peaks in PM_{10} at about the time of peak commuter traffic. The Los Angeles monitoring station showed higher PM_{10} concentrations in the morning and evening than at midday. Azusa and Long Beach monitoring stations showed broad daytime peaks. The Indio monitoring station showed an evening peak.

The weekday to weekend mean PM_{10} concentrations at all monitoring stations showed significantly lower concentrations on weekends (Hoggan et al., 1993). At the two SEDAB stations, Indio and Banning, Saturday PM_{10} concentrations were slightly lower than weekdays, but Sunday PM_{10} concentrations fell within the range of weekday means.

Some seasonal characteristics of the Los Angeles basin are depicted in Figure 6-84. The monitoring sites at different parts of the basin have markedly different seasonal concentration patterns. Hawthorne and Long Beach near the Pacific Coast and Burbank in an inland valley have the higher PM_{10} concentration in late fall and early winter (Figure 6-84b,c). On the

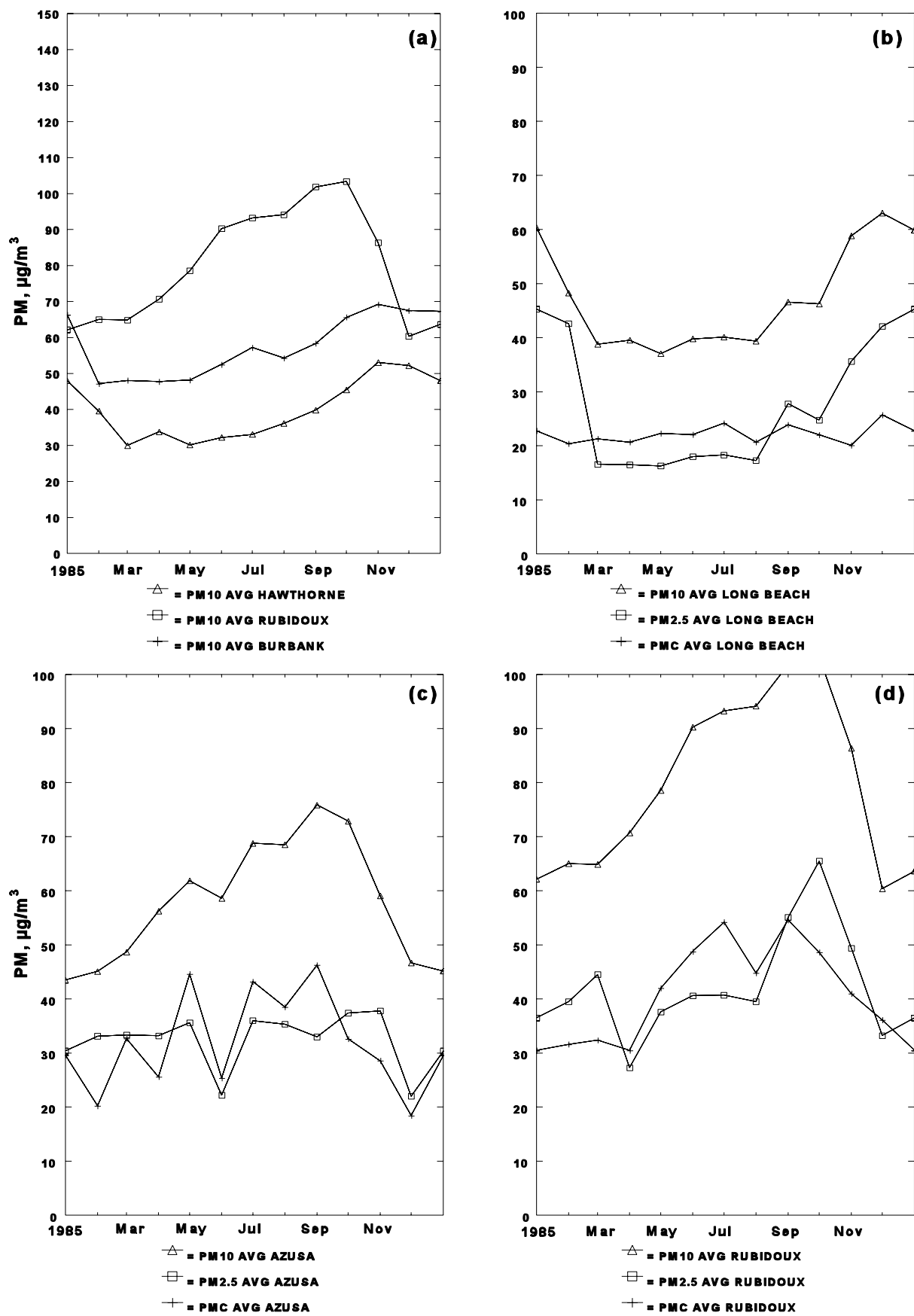


Figure 6-84a,b,c,d. Fine, coarse, and PM₁₀ seasonal patterns near Los Angeles. (Note scale for (a) is 150 $\mu\text{g}/\text{m}^3$.)

other hand, Azuza and Rubidoux in the eastern part of the basin exhibits the higher PM_{10} concentration during the May to October 'smog season' (Hoggan et al., 1993) (Figure 6-84b,d,e). The main causes of different seasonalities are likely to be associated with seasonally varying meteorological, transport, and chemical transformation patterns. The role of coarse and fine particles in the Los Angeles basin is also illustrated in Figure 6-84. At Long Beach, near the coast (adjacent to Hawthorne), the fine particles dominate the PM_{10} during the November through February winter season (40 to 50 $\mu\text{g}/\text{m}^3$). Coarse particles at Long Beach are constant throughout the year at about (20 $\mu\text{g}/\text{m}^3$). At Azuza and Rubidoux fine and coarse particles contribute roughly equally to the high PM_{10} concentrations. Thus, the PM_{10} aerosols over the smoggiest parts of the Los Angeles basin are not dominated by fine secondary aerosols but contributed by both fine and coarse particles.

The Rubidoux site in 1985 to 1988 showed violations of the 24-h PM_{10} standard approximately 12% of the time with a large contribution from ammonium nitrate (Chow et al., 1992c). A large group of dairies and animal husbandry operations in the Chino area approximately 13 km west of the Rubidoux site were identified as major ammonia emitters (Russell and Cass, 1986). To better evaluate the immediate area, measurements were made at the Rubidoux, Riverside-Magnolia, and Riverside sites. The results indicated that the Rubidoux site did represent urban-scale contributions of primary motor vehicle exhaust, secondary sulfate, and secondary nitrate. However, there also were significant neighborhood-scale and urban-scale contributions of primary geological sources and lime/gypsum sources contributing to the PM_{10} concentration (Chow et al., 1992c).

The Los Angeles smog has been the subject of extensive spatial, temporal, size and chemical composition studies since the 1960s (Appel et al., 1976, 1978, 1979; Hidy et al., 1980). A number of individual studies are discussed below.

The chemical characteristics of the PM_{10} aerosols were measured throughout 1986 (Solomon et al., 1989). Five major aerosol components (carbonaceous material, elemental carbon and organic carbon [measured value multiplied by 1.4 to account for O and H associated with C], nitrate, sulfate, ammonium, and soil-related materials, as measured) accounted for over 80% of the 1986 annual average PM_{10} mass. In all, measured chemical components were included from 80 to 94% of the PM_{10} mass was chemically identified. The nitrate and ammonium concentrations were substantially higher at the Rubidoux and Upland sites than at

other sites. Measurements made off the coast at San Nicolas Island suggest that from 28 to 44% of the annual average concentration at individual on-land sites can be associated with a regional background (Solomon et al., 1989).

More recently the LA aerosol characteristics during 11 summer days and 6 fall days in 1987 have been further elucidated by Southern California Air Quality Study (SCAQS) (Lawson, 1990). Several of the SCAQS studies reported are discussed below. The SCAQS study is also discussed in Chapter 3, Section 3.4.2.3.

Nitrate, sulfate, ammonium, and organic and elemental carbon were the most abundant species in the $PM_{2.5}$ fraction during SCAQS (Chow et al., 1994a). The coarse particle fraction was composed largely of soil-related elements (e.g., aluminum, silicon, calcium, iron) at the inland sites and with marine-related elements (e.g., sodium, chloride) at the coastal sites. Average concentrations for most chemical compounds were higher during the fall than during the summer, except for sulfate which was more abundant in summer. The $PM_{2.5}$ constituted one-half to two-thirds of PM_{10} at all sampling sites. $PM_{2.5}$ nitrate and ammonium concentrations were negatively biased for daytime samples compared to nighttime samples, consistent with diurnal changes in temperature and the effect of these changes on the equilibrium between particulate ammonium nitrate and gaseous ammonia and nitric acid. (Chow et al., 1994a; Watson et al., 1994a).

Wolff et al. (1991) measured the smog aerosol pattern during SCAQS at Claremont, CA, and Long Beach, CA, in the eastern and western Los Angeles basin, respectively. Claremont's air quality during the summer was characterized by high concentrations of photochemically produced pollutants including ozone, nitric acid, particulate nitrate, and particulate organic carbon (OC). The highest concentrations of these species were experienced during the daytime sampling period (0600 to 1800) and were associated with transport from the western part of the basin. Long Beach's air quality during the fall was characterized by frequent periods of air stagnation that resulted in high concentrations of primary pollutants including PM_{10} , OC and elemental carbon (EC) as well as particulate nitrate. Night-time levels of most constituents exceeded daytime levels due to poorer night-time dispersion conditions. At Claremont, OC and nitrate compounds accounted for 52% of PM_{10} , while at Long Beach they accounted for 67% of PM_{10} . On the average, there appears to be sufficient particulate ammonium to completely neutralize the nitrate and acidic sulfates.

In situ, time resolved analysis for aerosol organic and elemental carbon in Glendora, CA (Turpin et al., 1990), showed strong diurnal variations with peaks occurring in the daylight hours. Comparison of the diurnal profile of organic carbon with those of elemental carbon provided evidence for the secondary formation of organic aerosol in the atmosphere. Turpin et al. (1991) observed that secondary organic aerosol appears to have contributed roughly half of the organic aerosol in Pasadena during midday summer conditions.

Turpin and Huntzicker (1991) also found that the organic and elemental carbon concentrations exhibit strong diurnal variations. Peak concentrations occur during the daylight hours in the summer and at night in the fall. The maximum concentrations observed in the fall (maximum total carbon, $88 \mu\text{g}/\text{m}^3$) were two to three times higher than the summer maxima (maximum total carbon, $36 \mu\text{g}/\text{m}^3$). Measurements of elemental and organic carbon have been carried out by Gray et al. (1986). Extensive efforts have been made by Cass and coworkers (e.g. Rogge et al., 1993; Hildemann et al., 1991) to identify the molecular composition of the organic component. While some tracers have been identified, only a fraction of the organic PM has been characterized in terms of its molecular composition.

Gaseous nitric acid and fine particulate nitrate at Claremont, CA (Pierson and Brachaczek, 1988) both showed pronounced (~ 10 -fold) diurnal variations; however, coarse particles showed little diurnal variation. The average concentrations over the September 11 to 19 study period were for HNO_3 , $7.1 \mu\text{g}/\text{m}^3$; fine NO_3^- , $7.29 \mu\text{g}/\text{m}^3$; and coarse NO_3^- , $7.1 \mu\text{g}/\text{m}^3$. Fine NO_3^- may have been underestimated due to volatilization during or after sampling. This problem is discussed in Chapter 4, Section 4.2.10.1.

Careful size distribution measurements in the Los Angeles basin (John et al., 1990) shed light on the size spectrum dynamics for ammonium, sulfate and nitrate. Three modes, two submicron and one coarse, were sufficient to fit all of the size distributions. The smallest mode, at $0.2 \pm 0.1 \mu\text{m}$ aerodynamic diameter, is probably a condensation mode containing gas phase reaction products. A larger mode at $0.7 \pm 0.2 \mu\text{m}$ is defined as a droplet mode. Most of the inorganic particle mass was found in the droplet mode. The observed condensation and droplet modes characterize the overall size distribution in the 0.1 to $1.0 \mu\text{m}$ range, previously described by Whitby and coworkers as a single accumulation mode (Whitby et al., 1972; Whitby, 1978). Wall et al. (1988) also found that in September 1985 at Claremont, CA fine particle nitrate was

associated with ammonium, while coarse mode nitrate was associated with both ammonium and sodium. Sulfate was primarily in two submicrometer modes.

A clear demonstration of the effect of relative humidity and aerosol loading on atmospheric sulfate size distributions is given by Hering and Friedlander (1982). Days of high relative humidity and aerosol loading correspond to high mass median diameters ($0.54 \pm 0.07 \mu\text{m}$) for the sulfate while low relative humidity and low aerosol loadings correspond to small mass median diameters ($0.2 \pm 0.02 \mu\text{m}$). According to their interpretation, the larger ($0.54 \mu\text{m}$) sulfate particles resulted from aqueous phase reactions of SO_2 . The finer ($0.2 \mu\text{m}$) sulfate resulted from homogeneous gas phase reactions leading to the nucleation of sulfuric acid particles.

McMurry and Stolzenburg (1989) provide evidence that Los Angeles smog aerosols are externally mixed. Monodisperse ambient aerosols were often found to split into nonhygroscopic (no water uptake) and hygroscopic portions when humidified. An average of 30% of the particles in the 0.2 to $0.5 \mu\text{m}$ range were nonhygroscopic. However, the proportion of particles that were nonhygroscopic varied considerably from day to day and on occasion was 70 to 80% of the particles. The data show that for the hydrophilic aerosol, the larger particles (0.4 to $0.5 \mu\text{m}$) grew more when humidified than did smaller particles (0.05 to $0.2 \mu\text{m}$).

Size distributions of aerosol phase aliphatic and carbonyl groups at Claremont, CA (Pickle et al., 1990) showed maxima in the 0.12 to $0.26 \mu\text{m}$ and the 0.5 to $1.0 \mu\text{m}$ size functions. From the aliphatic carbon absorbency, the ambient samples generally showed maxima in the 0.076 to $0.12 \mu\text{m}$ size fraction. The authors attribute the carbonyl absorbance almost entirely attributed to products of atmospheric reactions and the aliphatic absorbencies in particles smaller than $0.12 \mu\text{m}$ to automotive emissions.

Cahill et al. (1990) found that the sulfate aerosol size at Glendora, CA, is smaller, $0.33 \mu\text{m}$ (MMD) during clear days compared to $0.5 \mu\text{m}$ on smoggy days.

The size distributions of organic nitrate groups in ambient Los Angeles aerosol were typically bimodal (Mylonas et al., 1991). During periods of high photochemical activity, the maxima in the mass loadings were in the 0.05 to $0.075 \mu\text{m}$ and the 0.12 to $0.26 \mu\text{m}$ size fractions. During periods of low-moderate ozone concentrations, the distributions were shifted to slightly larger sizes, with maxima appearing in the 0.075 to $0.12 \mu\text{m}$ and the 0.5 to $1.0 \mu\text{m}$ size fractions. A principal component analysis of the organonitrate loadings revealed strong correlations with ozone concentrations and with aerosol phase carbonyl loadings.

The analysis of coarse particles in Claremont, CA (Noll et al., 1990) show that the coarse particle mass could be divided into two categories: material that was primarily of crustal origin (Al, Ca, Fe, and Si) and material that was primarily of anthropogenic origin (Cd, Cu, Mn, Ni, Pb, and Zn). The mass of crustal material varied between 33 and 49% of the total coarse mass, while the mass of anthropogenic elements listed above were <1%.

The daily frequency distribution of the chemical components of the Los Angeles aerosol measured over a 1-year period were approximately lognormal (Kao and Friedlander, 1994). For nonreactive aerosol components, the geometric standard deviation (GSD) is nearly constant at 1.85 ± 0.14 even for components from different source types. An apparent bimodal frequency distribution for sulfates probably corresponds to the two differing reaction pathways by which gas-to-particle conversion occurs. However, the bimodal sulfate distribution function was not found at other Los Angeles sites (Kao and Friedlander, 1995). The authors suspect a relationship between GSD and the level of complexity of the stochastic physical and chemical processes affecting the distributions of the individual species. They also point out that the chemical concentration of the Los Angeles aerosol that corresponded to the peak in the (nearly) lognormal frequency distribution of the total mass is lower than the simple average chemical concentration.

A long term data base for organic and elemental carbon has been constructed (Cass et al., 1984; Gray et al., 1984). The average elemental carbon concentrations at seven monitoring sites in the Los Angeles area, for the 24-year period (1958 to 1982), were estimated to range from $6.4 \mu\text{g}/\text{m}^3$ at downtown Los Angeles to $4.5 \mu\text{g}/\text{m}^3$ at West Los Angeles. At most monitoring sites studied, elemental carbon concentration were lower in recent years than during the late 1950s and early 1960s.